Adsorption of Organophosphates from Drinking Water Using Activated Carbon from Seed Waste

Author: Caleb Isaac Mathias
Research Advisor: Dr. Veera M. Boddu
Academic Advisor: Dr. Thomas K. Mitchell

Conducted at the United States Department of Agriculture, Agriculture Research Station, National Center for Agriculture Utilization Research, 1815 N. University Street Peoria, IL 61604

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A B S T R A C T

A constant concern in modern agricultural production is pesticide runoff. Pesticides can leach into groundwater or be released into the atmosphere and return as contaminated rainwater. One method of mitigation is in the form of activated carbon, which possesses a net negative charge and functional groups which allow for the adsorption of chemicals from water. For this study, pyrolized seed was treated with phosphoric acid to increase the porosity of the char. This increased porosity leads to a greater surface area, and thus more room for the pesticide molecules to bind, which in this case were three commonly used organophosphates: parathion, malathion, and diazinon.

To test the adsorptive capacity of the acid-treated seed biochar, three organophosphates were prepared at various concentrations for batch and column adsorption experiments. Parathion, malathion, and diazinon were reacted with the biochar and samples were taken using a syringe with a 0.2μm filter then examined via HPLC analysis to determine the concentrations left in the solution by utilizing the area under the produced curve. These samples were also compared with those of a control activated carbon source, F300 carbon from Calgon. The pesticides were chosen due to their heavy usage in agriculture and the carbon source was chosen as it does not have as much literature surrounding it as the other sources of activated carbon do. Initial kinetic studies have shown that the acid-treated seed approached a concentration of 0.000 PPM at a faster rate than the F300 for parathion and diazinon, with the malathion solution reaching 0.5901 PPM at 24 hours for the acid-treated and 0.000 PPM for the F300.

1. Introduction

A constant concern in modern agricultural production based on the issue of runoff. Pesticides can leach into groundwater or be released into the atmosphere and return as contaminated rainwater (Kellogg et al. 2000). Not only is the drinking water affected, but aquatic life and those that feed on it are exposed to the contaminants as well. A higher risk of cancer, disruption of the endocrine and central nervous system, and even a risk of Parkinson's and Alzheimer's disease are possible health effects of pesticide exposure, whether this exposure is direct or accidental (Nascimento 2017). Over half of the streams and rivers tested by the National Water Quality Assesment (NAWQA) Program surpass their required benchmarks for pesticide content, and many of these samples contain a mixture of different pesticides (Gilliom 2007). Organophosphates are a well studied and widely applied pesticides commonly found in both agricultural and urban contaminated water sources (Uchimiya et al. 2012).

Organophosphates are a commonly used group of insecticides due to low cost and a large host range (Somsiri et al. 2009). Metal hydroxide and clay particles in soils can adsorb the pesticides and form Lewis acid complexes, and during hydrolysis can enhance the leaving ability of the ester (Uchimiya et al. 2012).

While the soil's organic matter can impact the mobility of pesticide residue, activated carbon in the form of biochar can also have a similar effect. There have been many tested sources, including chicken feather (Li et al. 2017), soybean hulls (Giri et al. 2017), pine tree sawdust (Zhao et al. 2017), and oak bark (Mohan et al. 2007). There have also been other methods, including ion exchange via zeolite (Huang et al. 2010), composite materials (Halim et al. 2010), and air stripping (Bonmatii and Flotats, 2003). But pyrolysis of agricultural waste products is seen as a favorable method due to the fact that it presents an economic advantage due the low cost and high disposal opportunity that it provides for the industry (Rodrigues et al. 2011).

The seed being used for this biochar is one such source of agricultural waste, but this product cannot be specified due to USDA policy. There is a significant amount of waste being produced that would benefit from an environmentally friendly means of disposal. The surface of the seed has been characterized after being cut, pyrolyzed, and treated with acid. It was found to have a high number of macrospores, mesopores, and micropores (Zhu et al. 2016); and Zhu and Kolar (2014) found the functional groups on the surface to be carbonyl (C=O), phenolic (-OH), and carboxylic groups (COOH), which proved very effective in the uptake of aqueous aluminum. The presence of such oxygen-containing functional groups gives a net negative charge to the surface of the biochar, providing an effective adsorbent for organic pollutants (Xu et al. 2011).

In order to help activation, a phosphoric acid treatment has been applied, as described by Elizalde-Gonzalez et al. (2007). The acid treatment aids in the formation of micropores, as well as increases pore volume and a 20-30% increase in C retention (Zhao et al. 2017). It also increases the specific surface area (SSA) due to acid catalysis and dehydration, as well as increased carbon retention. Zhao et al. (2017) cites a (65-70%) C retention level.

To test the adsorptive capacity of the acid-treated seed biochar, three organophosphates were prepared at various concentrations with batch and column adsorption experiments were performed. Parathion, malathion, and diazinon were reacted with the biochar and samples were taken to be examined via HPLC analysis. These samples were also compared with those of a control activated carbon source, F300 carbon from Calgon. The pesticides were chosen due to their heavy usage in agriculture and the carbon source was chosen as it does not have as much literature surrounding it as the other sources of activated carbon do. It has shown promising results in other studies (Zhu et al. 2016), however, and the hope is that this research will lead to water purification columns that will be used to filter pesticide residue out of water sources and fields.

2. Materials and Methods

Seed pits were obtained from a local Mexican restaurant. Following Zhu et al. 2016, the seeds were rinsed with DDW (distilled, deionized water) and left to dry at 50°C overnight. After being ground using a Thomas Digital ED-5 Wiley Mill (Thomas Scientific, Swedesboro, NJ) the biochar was separated into 0.6mm-1.2mm particles using a 16-30 mesh. It was activated using H_3PO_4 in a top-lit updraft gasifier stove (TLUD) referencing Peterson et al. 2014 and Evangelista et al. 2012. The control activated carbon, F300, was obtained from Calgon.

The water used was DDW with a resistivity of 1818MΩ-cm (Thermo Scientific Barnstead Nanopure, Waltham, MA). For HPLC analysis HPLC grade acetonitrile was obtained from Fisher Scientific (Fair Lawn, NJ) diluted to a 50% mixture using DDW. The three pesticides, parathion, malathion, and diazinon, were obtained from Sigma-Aldrich (Milwaukee, WI).

2.1. Equilibrium Determination

In order to better understand the adsorptive capacity of the F300 biochar compared to the acid-treated seed biochar, an equilibrium study was carried out for each pesticide. The F300 particles were placed in a 4 DR vial with 10ppm, 20ppm, 30ppm, and 40ppm solutions, each prepared in triplicate. A control containing 100 mL of DDW was also used, and each of the three vials were held together with rubber bands, wrapped in aluminum foil, placed in a sealed plastic bag, then placed in a 250 mL beaker, which allowed them to be securely placed in an incubator/shaker. They were shaken at 175 RPM at 25°C for six hours. They were then removed and a 1 mL sample was taken with a syringe and filtered into an HPLC vial using a 0.2µm Nylon filter. The HPLC vials were then placed in an HPLC machine and samples were taken every 30 minutes until all 13 vials had been extracted.

2.2 Sorption Kinetics

A 250 mL Erlenmeyer flask was filled with 0.1 g of F300 biochar and filled with 100mL of a 40ppm malathion solution. A second flask was also filled with 0.1g of F300 biochar and filled with a 140ppm Diazinon solution. This was repeated for the acid-treated seed biochar. These four flasks had a heavy layer of parafilm wrapped around their tops and were placed in a New Brunswick controlled environment incubator shaker (Edison, NJ) at 30°C for 8 hours, being removed every hour to have a sample taken and filtered into an HPLC vial using the syringe setup described in the equilibrium section. Once the 8 hours were over, the four flasks were left in the shaker until the next morning, where they continued to be sampled every hour for the next 8 hours for a total of 32 hours of incubation/shaking time.

2.3 Column Adsorption Experiments

A (mL) column was filled with (g) of biochar, being flushed into the column with water and using a copper wire to push down on the particles to ensure that they were settling evenly. Using a speed of 4.1 through a Master Flex pump (Cole Parmer, Vernon Hills, Il), the pesticide solution was passed through until 95 test tubes had been filled on a Frac-920 test tube rotator (GE Healthcare, USA).

3. Results

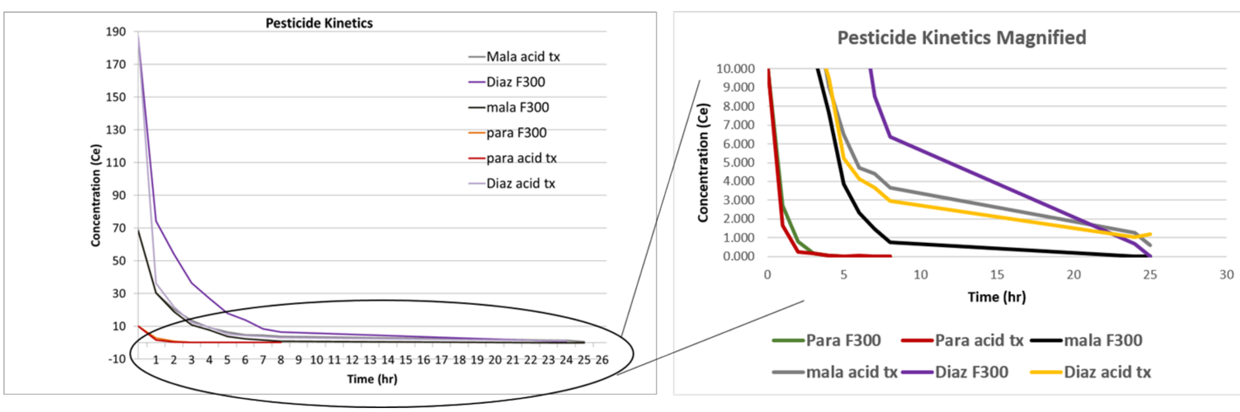

Figure 1. Initial kinetic studies have shown that the acid-treated seed approached a concentration of 0.000 PPM at a faster rate than the F300 for parathion and diazinon, with the malathion solution reaching 0.5901 PPM at 24 hours for the acid-treated and 0.000 PPM for the F300.

The seed-waste product has shown promising results. During equilibrium studies, the biochar had adsorbed the respective pesticides out of solution within the eight hour window, even at a slightly faster rate than the F300 control. When kinetic studies were performed (**Figure 1**) the biochar had also proven faster, save for the malathion. However, when preparing for the column studies (***Section 2.3***), it was revealed that even at less than half the solubility limits of each pesticide that they had been falling out of solution. After mixing for 24 hours with heat, gel bubbles were observed at the bottom of the volumetric flasks. What is more, the HPLC graphs had revealed some small breakdown products as well. Because this was only observed at this late stage, it is not believed that it had any major impacts on earlier studies, but now that the protocol has been streamlined and perfected, it would be the best course of action to consider revisiting some of the kinetic tests.

4. Conclusions

Seed waste product was pyrolized in an oven and treated with phosphoric acid. Initial studies have shown promising results for the seed waste as a source of biochar. When tested for the adsorption of organophosphates, it fared better than the control for two of the three pesticides used and had surpassed expectations in the equilibrium studies. It was only towards the end that the HPLC analysis that had been used started to detect unwanted breakdown products from the pesticide solutions, but the overall results are the same. It is hopeful that this product can be integrated into water treatment columns which can be used to filter contaminated water. It will also serve to combat continuously growing agricultural waste.

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